



(19)

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(11)

**EP 0 786 517 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**30.07.1997 Bulletin 1997/31**

(51) Int Cl.<sup>6</sup>: **C11D 3/37**

(21) Application number: **97200107.7**

(22) Date of filing: **16.01.1997**

(84) Designated Contracting States:  
**DE ES FR GB IT**

(30) Priority: **25.01.1996 US 591059**

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(54) **Detergent composition**

(57) Detergent composition comprising surfactant

material, an amphiphilic carboxy containing polymer  
and an uncharged polymer.

**EP 0 786 517 A1**

**Description**Technical Field

5 The present invention relates to polymer containing detergent compositions, process of preparing detergent compositions and washing methods using polymer material.

Background

10 Various types of polymers have been described in the art, e.g. U.S. Patent No. 5,147,576 to Montague et al. describes decoupling polymers in structured liquids.

WO 95/13354 (P&G) discloses composition comprising active, builder, fluorescent and polymer selected from PVPNO and N-vinyl pyrrolidone/N-vinylimidazole copolymers.

WO 94/10277 P&G discloses a composition comprising polyamine N-oxide polymer and terephthalate polymer.

15 WO 95/07336 P&G discloses granular products with active, builder, PVP-N-oxide polymer, specific PVP-VI polymer and specific sulphonated end-capped SRP.

EP 635,563, EP 635,565, WO 94/02576, WO 94/02580, WO 94/02581, WO 94/11473, WO 94/10277, WO 95/03390 and WO 95/33026 disclose compositions comprising N-containing polymers. Polycarboxylates are mentioned as optional ingredients.

20 EP 581,753 discloses N-containing compounds with polymeric polycarboxylate dispersing agents.

Polymers have been suggested for various purposes in the washing process. Anti-redeposition polymers are used to complex material in solution and prevent it from depositing on fabric. A special class of anti-redeposition agent are the dye transfer inhibiting polymers which complex dye molecules in solution and thus prevents deposition of colours on fabric.

25 Oily soil and particulate soil release polymers are polymers which change the characteristics of fabric. In order to be effective, they have to be deposited on the fabric surface before the fabric is stained.

We have however found a way to improve stain removal of detergent compositions, in particular the removal of particulate stains, and especially when embedded in an oily or fat matrix, by using a special polymer combination which provides synergistic stain removal benefits on these stains. Examples of such stains are make-up, lipstick and shoe polish.

30 In addition, we have found that the combination of the polymer combination can be stably incorporated into aqueous isotropic liquid detergent compositions.

Statement of the Invention

35 Consequently, the invention is directed to detergent compositions comprising surfactant material, an amphiphilic carboxylate containing polymer and an uncharged polymer.

The present invention is further directed to aqueous liquids comprising the particular polymer combination of an amphiphilic carboxylate containing polymer and an uncharged polymer.

40 The present invention is further directed to a method of preparing a liquid detergent composition comprising the polymer combination of the invention by mixing the ingredients.

The present invention is further directed to a method of washing fabrics by adding the polymer combination of the present invention to the wash liquor.

45 Amphiphilic carboxy containing polymer

Preferably, the amphiphilic carboxy containing polymers comprise monomers comprising a carboxy group, said monomers being preferably selected from carboxylated sugar units, carboxylated unsaturated units (like acrylate, methacrylate, itaconate, maleate and mixtures) and mixtures thereof. The amphiphilic carboxy containing polymer preferably also contains monomer units which are uncharged. Preferably, these uncharged monomers are selected from vinylacetate, vinylpyrrolidone, vinylpyridine, vinylimidazole, styrene, alkyl-esters of the above carboxylate monomers (e.g. 1-20 alk(en)yl, preferably C5-16 alkyl) and mixtures thereof.

50 More preferably, the amphiphilic carboxy containing polymers are of the following type: polyacrylate, styrene-acrylate copolymer, acrylate-alkylmethacrylate copolymers, ethoxylated methacrylate-acrylate copolymer, methacrylate-vinylacetate copolymer or itaconate-vinylacetate copolymers. Examples of such polymers are Narlex LD55, Narlex H100, Narlex H1200 and Narlex DC1 (ex National Starch).

55 Additionally, the amphiphilic carboxy containing polymers may preferably be copolymers of ethoxylated maleate and dodecene-1. An example thereof is Dapral GE 202. Optionally, the amphiphilic carboxy containing polymer is partly

ethoxylated, e.g. with a PEG 350 side chain.

Most preferably, the amphiphilic carboxy containing polymers are selected from copolymers of acrylic acid and styrene. Examples are Narlex H100 and Narlex H1200 (ex National Starch).

Preferably, the amphiphilic carboxy containing polymer is present at a level of from 0.05 to 5% by weight of the composition, more preferably from 0.1 to 2, most preferably from 0.2 to 1.5, for instance at a level of 0.5% by weight of the composition.

The ratio of carboxy containing hydrophilic monomers to uncharged monomers can vary in a broad range e.g. from 100:1 to 0.5:1, preferably from 50:1 to 1:1. For copolymers of acrylic acid and styrene this ratio is preferably between 10:1 and 0.5:1, most preferred from 6:1 to 1:1.

#### Uncharged polymer

Preferably, the uncharged polymer material is selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinylloxazolidone, polyvinylimidazole and mixtures thereof.

#### a. Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use contain units having the following structure formula: R-Ax-P, wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both. A is NC(O), C(O)O, -O-, -S-, -N-; x is 0 or 1; R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic group or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general quaternary N-structure: (R<sub>1</sub>)<sub>x</sub>-N(-O)(R<sub>3</sub>)<sub>z</sub>(R<sub>2</sub>)<sub>y</sub> and =N(O)(R<sub>1</sub>)<sub>x</sub>, wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x and/or y and/or z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1,000,000. More preferably from 1:4, most preferably from 1:7 up to 1,000,000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a pKa<10, preferably pKa<7, more preferably pKa<6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water solubility.

Typically, the average molecular weight is within the range of 500 to 100,000; preferably from 1,000 to 50,000.

more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

#### b. Copolymers of N0-vinylpyrrolidone and N-vinylimidazole

5 The N-vinylimidazole N-vinylpyrrolidone polymers which may be used in the present invention have an average molecular weight range from 5,000 to 1,000,000, preferably from 20,000 to 200,000. Highly preferred polymer for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

10 The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J. W. Chemical Analysis VOl 113, "Modern methods of polymer characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000, more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

15 The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

#### c. Polyvinylpyrrolidone

20 Detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000 and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12. Polyvinylpyrrolidones will be known to persons skilled in the detergent field; see for example EP-A-262,897 and EP-A-256,696.

#### d. Polyvinylloxazolidone

30 Detergent compositions of the present invention may also comprise polyvinylloxazolidone. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably to 200,000, more preferably to 50,000 and most preferably to 15,000.

#### e. Polyvinylimidazole

35 Detergent compositions of the present invention may also comprise polyvinylimidazole. Said polyvinylimidazoles have an average molecular weight range from 2,500 to 400,000, preferably to 200,000, more preferably to 50,000, and most preferably to 15,000.

40 Preferably, the uncharged polymers are selected from ethoxylated ethylene-amine polymers, vinylpyrrolidone polymers, 2-vinylpyridine N-oxide containing polymers, vinylpyrrolidone-vinylacetate copolymers, vinylpyrrolidone-styrene co-polymers and vinylpyrrolidone-vinyl imidazole copolymers. Examples of such polymers are ethoxylated tetra-ethylenepentamine, polyvinylpyrrolidone K15, polyvinylpyrrolidone vinylacetate (PVP/VA S-630), polyvinylpyridine N-oxide, polyvinylpyrrolidone-styrene (Antara 430) and polyvinylpyrrolidone-vinylimidazole (Sokalan HP56). Most preferably, the uncharged polymers are selected from vinylpyrrolidone (PVP), polyvinylpyridine N-oxide and copolymers of vinylpyrrolidone and vinylimidazole (PVP-PVI). An example is Sokalan HP 56 (ex BASF).

45 Preferably, the level of the uncharged polymer is from 0.1 to 3%, more preferably from 0.25 to 1.5%, for instance 0.5% by weight of the composition.

#### Detergent composition

50 Preferably, the detergent composition comprises surfactant material. Preferably, liquids according to the present invention comprise anionic surfactants at a level of 5% by weight of the composition or higher.

55 In a preferred embodiment of the invention, the surfactant comprises one or more of the surfactants selected from alkyl benzene sulphonate and sugar based surfactants. Sugar based surfactants are preferred. We have found that the use of these surfactants further improves the stain removal of the particulated stains in a fatty or oily matrix.

Liquid detergent composition

Preferably, the polymer combination is included in liquids, more preferably aqueous liquids. We have found that the polymers can in particular be useful in isotropic liquids as the liquid remains clear after addition of the polymer.

5 Another preferred embodiment of the invention relates to the use of the polymers in structured liquid detergent compositions, for example containing a structure of lamellar droplets of detergent active material.

Therefor, a particular embodiment of the invention relates to isotropic liquids comprise a liquid system which comprises surfactant material, electrolyte, hydrotrope, water and optionally monoethanolamine and/or triethanolamine. We have found that the polymer combination of the present invention is soluble in such liquids, in particular when the

10 ingredients are present at the levels at specified hereunder.

Therefor another particular embodiment of the invention relate to a structured liquid detergent composition comprising surfactant material and the polymer combination of the invention.

Surfactant material

15

Compositions of the invention may also comprise surfactant materials, preferably at a level of at least 5% by weight of the composition, more preferred at least 10% by weight, most preferred at least 20% by weight and in particular at least 25% by weight of the composition; and preferably at a level of at most 60% by weight, more preferably at most 50% and most preferably at most 45% by weight of the composition.

20 In the widest definition the surfactant material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache,

25 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkyl oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C<sub>6</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-di-amine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

30 Preferably, the composition then comprises at most 25%, more preferably at most 20%, most preferably at most 15%, in particular at most 10% by weight of the total ethoxylated nonionic surfactants of long chain EO (ethylene oxide) nonionic surfactants. Long chain EO nonionic surfactants are defined as comprising 15 or more EO groups, preferably 10 or more EO groups, more preferably 8 or more EO groups per nonionic molecule. It is noted that commercially available ethoxylated nonionics always represent a nonionic mixture.

35 Preferably the level of nonionic surfactant materials is from 1 to 40% by weight of the composition, more preferred from 2 to 20%.

40 Compositions of the present invention may contain synthetic anionic surfactant ingredients, which are preferably present in combination with the above mentioned nonionic materials. Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic surfactant compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>) benzene sulphonates; sodium alkyl glycerol ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C<sub>8</sub>-C<sub>18</sub>) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived from reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which

45 term is used to describe the material made by reacting olefins, particularly C<sub>10</sub>-C<sub>20</sub> alpha-olefins, with SO<sub>3</sub> and then neutralizing and hydrolysing the reaction product. The preferred anionic surfactant compounds are sodium (C<sub>11</sub>-C<sub>15</sub>) alkyl benzene sulphonates and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl sulphates.

Generally the level of the above mentioned non-soap anionic surfactant materials is from 1-40 % by weight of the composition, more preferred from 2 to 25%.

It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, alk(en)yl succinate for example dodecyl succinate, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used.

5 Preferably the level of soap in compositions of the invention is from 1-35% by weight of the composition, more preferred from 5-25%.

Surprisingly, we have found that inclusion of sugar based surfactants (preferably alkylpolyglycosides and/or polyhydroxy fatty acid amide surfactants) and/or alkyl benzene sulphonate (as described above) further improve the particulate stain removal characteristics of the polymer combination of the present invention. Suitable nonionics include

10 aldobionamides such as are taught in U.S. Patent No. 5,296,588 to Au et al. and polyhydroxyamides such as are taught in U.S. Patent No. 5,312,954 to Letton et al., both of which are incorporated by reference into the subject application.

Preferably, the level of the sugar based surfactants is from 0 to 20%, more preferably up to 15%, most preferably up to 10% and more preferably higher than 1%, most preferably higher than 3% by weight of the composition.

Alkylpolysaccharides have been disclosed US 4,565,647 and have a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g. glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g. between

20 the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 18 preferably from 10 to 16 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups. Suitable alkylpolysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglycosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglycosides and tallow alkyl tetra-, penta-, and hexaglycosides.

Preferred alkylpolyglycosides have the formula:

30  $R_2O(C_nH_{2n}O)_t(glycosyl)_x$ , wherein  $R_2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms;  $n$  is 2 or 3, preferably 2;  $t$  is from 0 to 10, preferably 0; and  $x$  is from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula:  $R_2-C(O)-N(R_1)-Z$  wherein  $R_1$  is H, or  $R_1$  is C1-4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof,  $R_2$  is C5-31 hydrocarbyl, and  $Z$  is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably,  $R_1$  is methyl,  $R_2$  is a straight C11-15 thereof, and  $Z$  is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

#### 40 Electrolyte material

Compositions according to the invention preferably comprise electrolyte material, some or all of which may be builder material. Preferably the total level of electrolyte is from 1 to 60% by weight of the composition, more preferred 1 to 30%, most preferred 1 to 10%.

45 Preferably, electrolyte material comprises material selected from citrate, borate, sulphate, carbonate, bicarbonate, propionate, formate, chloride, phosphate, silicate and mixtures thereof.

It is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. In this context it should be noted that some surfactant materials such as for example soaps, also have builder properties.

50 Examples of phosphorous containing inorganic detergency builders include the water-soluble salts, especially alkali metalpyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used. It may however be preferred to minimise the amount of phosphate builders.

55 Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted

ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine-tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate mono succinate, tartrate di succinate and citric acid. Citric acids or salts thereof are preferred builder materials for use in compositions of the invention.

#### Hydrotrope material

Preferably isotropic compositions according to the invention comprise hydrotrope material.

Preferably the hydrotrope material is selected from lower aliphatic alcohols, ethers of diethylene glycol and lower monoaliphatic monoalcohols. Specifically, ethanol, n-propanol, iso-propanol, butanol, polyethylene glycol, propyleneglycol, dipropylene glycol, hexylene glycol, methoxyethanol, ethoxyethanol, butoxyethanol, ethyldiglycolether, benzylalcohol, butoxypropanol, butoxypropoxyethanol, butoxypropoxypropanol, 1,2 propanediol, sorbitol and glycerol. Preferably the solvent system comprises propyleneglycol and/or ethanol.

Preferably the level of the hydrotrope material in isotropic systems is from 5 to 25%, more preferably from 7 to 20% by weight of the composition. Structured liquid compositions according to the invention preferably comprise no or only low levels of hydrotrope material, eg. 0 to 5 wt%.

#### Water

Preferably, the liquid compositions of the present invention are concentrated. Therefore, the water level in the liquid detergent compositions according to the present invention is preferably at most 70%, more preferably at most 60, most preferably at most 55% by weight of the composition. Preferably, the liquid system comprises at least 10%, more preferably at least 15%, most preferably at least 20% by weight of the composition.

#### Monoethanolamine and Triethanolamine

The liquid system of the compositions according to the invention optionally contain one or more compounds selected from monoethanolamine and/or triethanolamine at a level of from 0 to 10% by weight of the composition.

#### Optional ingredients

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo), enzyme stabilizers, anti-redeposition agents, germicides and colorants. Obviously in selecting the materials other than the polymer for use in compositions of the invention, also biodegradable materials are preferred for environmental reasons.

#### Product form

As has been indicated, liquids which are isotropic or structured are well-known in the art.

Liquid compositions of the invention preferably have a viscosity of less than 2,500 mPas at 21 s<sup>-1</sup>, more preferred less than 1,500 mPas, most preferred less than 1,000 mPas and preferably higher than 100 mPas at 21 s<sup>-1</sup>.

Liquid compositions according to the invention are physically stable. In the context of the present invention, physical stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation.

Preferably, the liquid compositions according to the invention have a product pH of at least 6, more preferably at least 6.5, most preferably at least 7 and preferably at most 14, more preferably at most 12, most preferably at most 10.

Preferably the pH, as provided to the wash liquor, is at least 6, more preferably at least 7.5, most preferably at least 8. Preferably the pH is at most 12, more preferably at most 10, most preferably at most 9.

Method of preparation

Liquid compositions of the invention may be prepared by any conventional method for the preparation of liquid detergent compositions. A preferred process of preparation is illustrated in the examples. Such processes lead to preparation of clear isotropic liquids.

The invention will be illustrated by way of the following non-limiting Examples.

ExamplesExample 1

The following formulation was prepared by adding the ingredients in the order listed to some water:

Composition		
Ingredients	A	1
Na-citrate (37.5%)	13	13
Propyleneglycol	6	6
Premix of 10% water/70% sorbitol/borax	19.5	19.5
NaOH (50%)	1.6	1.6
Alkyl Benzene Sulphonate	7.8	7.8
Nonionic (Neodol) (wait until temperature is lower than 32°C)	8	8
Alkyl Ether Sulphate (59%)	23.8	23.8
Minors (adjust pH to 7 with NaOH)	1.5	1.5
Water	up to 100	up to 100
Polymer Narlex H1200	-	0.25
Polymer PVP/PVI (Sokalan HP 56)	-	0.5

Tests cloths with particulate stains (e.g. mascara, curry, make-up, shoe polish and clay) were washed with the above compositions. The composition according to the invention showed better stain removal as evidenced by the higher Delta R reflectance.

Narlex H100 and Alco 2499 both have similar effects when included in the above composition instead of Narlex H1200 and replacing PVP-PVI with PVP also leads to similar results.

Example 2

The following formulation was prepared:

Ingredients	2 (% by weight)
Na-citrate (37.5%)	10.7
Propyleneglycol	7.5
Premix of water/sorbitol/borax	19.5
MEA	0.5
Cocofatty acid (mix for 15 minutes)	1.7
NaOH (50%)	2.2
Alkyl Benzene Sulphonate	10.3
Nonionic (Neodol) (wait until temperature is lower than 32°C)	6.3
Alkyl Ether Sulphate (59%)	12.9
Minors (adjust pH to 7 with NaOH)	1.3
Water	up to 100
Polymer Narlex H100	0.25
Polymer PVP K15	0.5

The polymer was added on top. The resulting liquid is clear and is stable upon storage.



Example 3

The following formulation was prepared:

5	Ingredient	3
	Borate	3
	Propylene glycol	8
	NaOH/KOH (50%)	9.2
10	Cocofatty acid (mix for 15 minutes)	14
	Premix of LAS and Neodol (mix during 5 minutes)	18.2
	Minors	1
	Water	up to 100
15	Polymer Narlex H100	0.25
	Polymer PVP K15	0.5
	pH:	about 8.8

20 The polymer was added on top. The resulting liquid is clear and is stable upon storage.

Example 4

25 The formulation of Example 1 was prepared with two other polymers, ie. with Narlex H100 and PVP K15. The resulting liquid was clear and stable upon storage.

**Claims**

- 30 1. Detergent composition comprising surfactant material, an amphiphilic carboxy containing polymers and an uncharged polymer.
2. Composition according to claim 1, wherein the amphiphilic carboxy containing polymer comprises uncharged monomers selected from:  
35 vinylacetate, vinylpyrrolidone, vinylpyridine, vinylimidazol, styrene, alkyl-esters of acrylate, alkyl-esters of methacrylate, alkyl-esters of itaconate, alkyl-esters of maleate and mixtures thereof.
3. Composition according to claim 1, wherein the amphiphilic carboxy containing polymer comprises hydrophilic monomers selected from acrylate, methacrylate, itaconate, maleate and mixtures thereof.
- 40 4. Composition according to claim 1, wherein the uncharged polymer is selected from is selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinylloxazolidone, polyvinylimidazole and mixtures thereof.
- 45 5. Composition according to claim 1, wherein the composition comprises a liquid system.
6. Composition according to claim 5, comprising from 5-60% by weight of surfactant, 1-60% by weight of electrolyte, 10-70% by weight of water and optionally 0-10% by weight of one or more compounds selected from monoethanolamine and triethanolamine.
- 50 7. Method of preparing a liquid detergent composition according to claim 5 by mixing the ingredients.
8. Method of washing fabrics by adding the detergent composition of claim 1 to the wash liquor.

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European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 0107

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 413 616 A (COLGATE PALMOLIVE CO) 20 February 1991 * page 11, line 44 - line 53; claims 1-20 * page 6, line 3 - page 7, line 39 *	1,5,7,8	C11D3/37
A	---	2,3	
X	EP 0 523 950 A (ROHM & HAAS) 20 January 1993 * page 3, line 51 - line 58; claims 1-11 * * table II *	1-3,5,7,8	
A	---	6	
D,X	EP 0 581 753 A (PROCTER & GAMBLE) 2 February 1994 * page 5, line 17 - line 24; claims 1-19 *	1-4,8	
X	WO 95 00611 A (VERONA INC) 5 January 1995 * page 2, line 17 - line 37; claims 4-6 *	1-7	
D,A	WO 95 33026 A (PROCTER & GAMBLE) 7 December 1995 * claims 1-10 *	4	
A	EP 0 459 077 A (LION CORP) 4 December 1991 * page 5, line 52 - page 6, line 16; claims 1-10 *	2,3,6	C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 April 1997	Examiner Ainscow, J
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application I: document cited for other reasons &: member of the same patent family, corresponding document			

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